Molecular composition of the water-soluble fraction of atmospheric carbonaceous aerosols collected during ACE-Asia

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[1] During the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia), samples of carbonaceous aerosols were collected on board the Center for Interdisciplinary Remotely Piloted Aircraft Studies (CIRPAS) De Havilland DHC-6 Twin Otter aircraft. The samples were analyzed to determine their total carbon (TC) and water-soluble organic compound (WSOC) contents as well as to identify the individual compounds comprising the WSOC fraction of the aerosol. The TC concentrations varied from 3.5 to 14.3 μg C m^{-3}; the highest TC levels were observed for samples collected in pollution layers that originated over mainland China. WSOC concentrations ranged from 0.54 to 7.2 μg C m^{-3}, with the WSOC fraction contributing from 10 to 50% of the carbon mass. About 50% of the carbonaceous aerosol mass in pollution layers could be attributed to WSOC. For samples collected in dust layers the WSOC fraction of TC was much lower than that observed in pollution layers. The sum of all the detected organic ions accounted for 6.9–19% of the WSOC. In the six samples collected by the Twin Otter during ACE-Asia, of the organic ions identified in the WSOC fraction, oxalate had the highest concentration. Samples collected from pollution layers exhibited a slightly higher ratio of formate to oxalate as compared to the other samples. Two samples had a relatively high ratio of lactate to oxalate, which might be a signature of some currently unidentified source of carbonaceous aerosol. The sum of the masses of sulfate and nitrate ions exceeded the sum of the masses of the identified organic ions by a factor of 9 to 17. The chemical levoglucosan, a tracer for biomass burning, comprised from 0.1 to 0.4% of TC mass. Comparing this ratio to the ratio measured directly in wood-burning studies it was determined that biomass burning may have represented from $\approx$2 to 10% of the carbonaceous aerosol collected during ACE-Asia. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* water-soluble organic compounds, dicarboxylic acids, airborne sampling

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1. Introduction

[2] A series of Aerosol Characterization Experiments (ACE) have been conducted which utilize ground, sea and aircraft-based measurements, satellite observations and atmospheric modeling with the goal of improving the prediction of climate forcing due to aerosol particles [*Bates et al.*, 1998; *Raes et al.*, 2000]. The third in this series of experiments is ACE-Asia, the intensive field measurement component of which was conducted from 31 March through 1 May 2001 [*Huebert et al.*, 2003]. One of the principal goals of ACE-Asia was to determine the chemical and physical properties of atmospheric aerosol originating from the Asian continent, including the levels of carbonaceous compounds. Carbonaceous material influences the optical

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properties, hygroscopicity, and ability of particles to act as CCN. Particulate carbon is often classified into three broad categories: carbonate carbon (CC), so-called elemental carbon (EC), and organic carbon (OC). EC is formed during the combustion of hydrocarbons and is a major light absorbing component of atmospheric particles. OC is either emitted directly to the atmosphere (primary emissions) or formed by the condensation of products from the atmospheric oxidation of volatile organic compounds (secondary OC). Typically, OC comprises 10–50% of the mass concentration ($\mu g\ m^{-3}$) of atmospheric aerosols [*Seinfeld and Pandis*, 1998]. Attaining a full molecular identification of the organic fraction of atmospheric particulate matter has proved to be one of the most challenging problems in atmospheric chemistry; indeed, because of the extremely large number of compounds and the difficulty of separating them for individual identification, it has not been possible to attain a complete organic molecular speciation for typical atmospheric particles.

[3] There exist a number of recent studies of the organic molecular composition of atmospheric particles in different regions (Table 1). A fraction of organic atmospheric particulate matter that is of special interest is that of water-soluble organic carbon (WSOC). Knowledge of the WSOC fraction is important in assessing the organic contribution to the hygroscopic behavior of particles and in understanding possible effects of the organic fraction on the surface tension of the particles and their activation to form cloud droplets (Table 2) [*Charlson et al.*, 2001].

[4] Dicarboxylic acids are an important identified component of particulate organic material [*Saxena and Hildemann*, 1996; *Schauer et al.*, 1996; *Kawamura et al.*, 1996a, 1996b, 2003; *Kawamura and Sakaguchi*, 1999]. Direct emission of dicarboxylic acids does not seem to be their predominant source; rather, these compounds appear to result largely from atmospheric chemical processes. The molecular paths by which these compounds are produced in the atmosphere have yet to be firmly identified. A recent study suggests that in-cloud oxidation processes may provide a route for production of oxalic acid [*Warneck*, 2003].

[5] As a component of ACE-Asia, the current study had the following goals: (1) determination of the WSOC fraction of organic carbon present in airborne particulate matter; and (2) identification and quantification the concentration of individual organic compounds comprising WSOC.

2. Aircraft Sampling Platform and Sample Collection

[6] Samples were collected on board a modified De Havilland DHC-6 Twin Otter aircraft operated by the Center for Interdisciplinary Remotely Piloted Aircraft Studies (CIRPAS). A total of 19 Research Flights (RFs) were conducted between 31 March and 1 May 2001 [*Huebert et al.*, 2003]. The center of aircraft operations was located at the Marine Corps Air Station (MCAS) Iwakuni, Japan, and the sampling area included portions of the Sea of Japan south and east of the Korean Peninsula, the East China Sea between China, Japan and Korea, and the Philippine Sea south of Japan. The sampling area is illustrated nicely in Figure 1 of *Gao et al.* [2003]; these authors also sampled aboard the Twin-Otter aircraft during ACE-Asia.

[7] Depending on the scientific goals of a mission, one or more flight profiles were used: (1) level legs at a particular altitude; (2) spiral ascents and descents between altitudes of 50 m and 3000 m; and (3) level descents from 3000 m to 50 m. Because of the need to collect sufficient particulate material so as to exceed the detection limits of the analytical method, sampling was conducted throughout an entire mission; therefore samples are integrated over the several different legs (and altitudes) of a given flight.

[8] Two inlets were mounted on the Twin Otter, one on the roof of the aircraft and a second mounted in the nose. The nose-mounted inlet was dedicated to sampling carbonaceous aerosols and designed to sample air isokinetically at an airspeed of 50 m s^{-1}. This inlet was constructed entirely of metal and could be removed from the aircraft and cleaned between flights if necessary. A manifold was used to separate the sample air among the three denuder samplers, while maintaining isokinetic flow conditions. The manifold included two impactors to remove cloud droplets from the sample air leading to the low-flow denuder samplers (samplers A and B in Figure 1). A third impactor was a component of the high-volume particle trap impactor-denuder sampler (sampler C in Figure 1). Samples were collected for analysis of their WSOC content using sampler C. For the particle trap impactor present in sampler C (Figure 1), the aerodynamic diameter of particles collected with 50% efficiency (d_{50}) was 7 μm [*Mader et al.*, 2001]. The compartment housing the denuder samplers was neither heated nor pressurized during flights. The temperature was monitored during flights using a temperature probe located in the samplers' flow controller. The inlet and manifold were made entirely of aluminum, and the transfer lines connecting the manifold to the denuder samplers were aluminum (sampler C) or copper (samplers A and B); no organic materials were in contact with the sample air throughout the entire system.

[9] Carbonaceous aerosol particles were collected using a high-volume particle trap impactor-denuder sampler [*Mader et al.*, 2001] (sampler C). The high-volume particle trap impactor-denuder sampler was operated with a pair of front and backup QFFs (19.4 cm diameter), at a flow rate of 300 Lpm. Flow through the denuder sampler was controlled using a volumetric flow controller interfaced to an onboard computer; samplers could be turned on/off at any point during the flight. During air sampling, the volumetric flow, pressure, and temperature of the sample air downstream of the filters were monitored at one-minute intervals. The flow controller had an accuracy of 0.5% and a precision of 1%. While in transit to the sampling site, there was no flow through the denuder samplers so as to prevent contamination of the samples.

[10] At the MCAS-Iwakuni, filters were prepared in a room for which an air purifier containing a HEPA filter and activated carbon filter was used to reduce the levels of volatile organic compounds (VOC) and ambient particles. Prior to sampling, QFFs were precleaned by baking at 550°C in a muffle furnace for 12–16 hours. QFFs were removed hot from the muffle furnace and immediately loaded into the denuder samplers. After loading a denuder sampler with filters, the inlet and outlet of the sampler were capped with Swagelok™ fittings to prevent airflow through the denuder samplers prior to sampling. The average OC

Table 1. Recent Studies of Organic Composition of Atmospheric Particulate Matter

Location	Date	Compounds Identified	Reference
Chichijima Island (27°04′N, 142°13′E)	April 1990 to Nov. 1993	C_2-C_{11} dicarboxylic acids (straight chain, branched keto-, and unsaturated)	*Mochida et al.* [2003]
Toronto area	1998/1999	alkanoic acids; acids; alkanes, PAHs	*Blanchard et al.* [2002]
Indian Ocean MBL	Feb./March 1999	dicarboxylic acids; hydroxylated dicarboxylic acids; alkanes; PAHs	*Neusüss et al.* [2002]
Jungfraujoch, Switzerland (3580 m asl)	summer 1998	WSOC: 2 fractions: (1) highly polyconjugated, acidic compounds, (2) slightly polyconjugated, neutral, very hydrophilic	*Krivacsy et al.* [2001a]
Mace Head, Ireland	July 1998 to Sept. 1999	oxalic and malonic acids (~14% of WSOC on a C basis)	*Kleefeld et al.* [2002]
Kpuszta, Hungary	Jan.–Sept. 2000	total carbon (≤1.5 μm diameter) and WSOC; polyols; polyacids; humic, fulvic acids	*Kiss et al.* [2002]
Southeast Asia	1997	oxalic, malonic, succinic acids; total diacids 2–8% of WSOC.	*Narukawa et al.* [1999]
Central Africa	Nov. 1996	formate; acetate; oxalate.	*Ruellan et al.* [1999]
Rondônia, Brazil	Oct. 1999	neutral compounds, mono- and dicarboxylic acids, polycarboxylic acids (~70% of WSOC identified)	*Mayol-Bracero et al.* [2002]
Melpitz, Germany	April/May 2001	polyhydroxy-, mono-, and dicarboxylic acids, polyols, sugars	*Carvalho et al.* [2003]
Hyytiälä forest, Finland	Aug. 2001	polyhydroxy-, mono-, and dicarboxylic acids, polyols, sugars	*Carvalho et al.* [2003]
St. Croix	June 2000	aliphatic and carbonyl C 60–90% of hygroscopic TOM in free troposphere; 20–50% hydrophobic TOM in marine boundary layer	*Maria et al.* [2002]

and EC loading on field blank filters was 0.30 and 0.12 μg C cm^{-2}, respectively. The OC blank value was similar to the 0.43 μg C cm^{-2} average blank value reported in the ACE-Asia OC/EC thermal-optical method interlaboratory comparison study reported by *Schauer et al.* [2003]. The EC blank value appears larger than the 0.05 μg C cm^{-2} value reported in the intercomparison, however this value has an uncertainty of 0.2 μg C cm^{-2}; the two values are not significantly different. Field blank filters were prepared in the same batch of filters as the filters used to collect samples, a field blank was loaded into the sampler, the sampler sealed to prevent the flow of air through the system and the filter allowed to sit in the sampler for approximately 30 min, removed and stored in the same fashion as the filter used during sampling.

[11] Immediately prior to sampling, filters were loaded into the sampler using stainless steel forceps. Sampling times depended on the particle mass concentrations measured at the sampling site and the overall goal of the particular RF, and ranged from 109 to 284 min. When the aircraft returned from a flight, the samplers were immediately returned to the filter handling room and filters unloaded from the samplers and placed into individual aluminum-lined petri dishes. The aluminum liners had been prebaked under the same conditions as the QFFs. For each sampling event, blank QFFs were loaded into filter holders, removed, and stored with the other samples. The forceps and aluminum liners had been precleaned by baking at 500°C in a muffle furnace for 12 hours. Samples were stored in a freezer until analysis.

3. Carbon Analysis

[12] OC, EC, CC, and TC concentrations of the material deposited on the filters were determined using a thermo-optical OC/EC analyzer (Sunset Laboratories, Forest Grove, Oregon) [*Birch and Cary*, 1996]. Briefly, a 1.45 cm^2 punch of a QFF was loaded into the thermo-optical OC/EC analyzer. Two different temperature programs were employed: (1) the ACE-Asia temperature profile and (2) the Total-C temperature profile. The ACE-Asia temperature profile was one employed by several participants in ACE-Asia for analysis of OC and EC. For QFF samples, OC and EC were determined as follows: OC was evolved under a stream of ultrahigh-purity He while heating the sample in four temperature steps of 1 min at 310°C, 1 min at 450°C, 1 min at 575°C, and 1.5 min at 870°C. To evolve EC and pyrolized OC, the sample was heated under a mixture of 10% O_2, 90% He in six temperature steps of 0.75 min at 550°C, 0.75 min at 625°C, 0.75 min at 700°C, 0.75 min at 775°C, and 0.75 min at 850°C, and 2.0 min at 900°C.

[13] TC was also measured using a second temperature profile termed the Total-C temperature program. The method was found to be more effective for determining TC and was not used to determine OC and EC. The Total-C method was as follows: TC was evolved from 2–3 pieces of

Table 2. Summary of WSOC/TC and WSOC/OC Ratios Reported in the Literature

Investigators	Location	Site Characteristics	Sample	Time Period	WSOC/TC	WSOC/OC	Number of Samples
Cadle and Groblicki [1982]	Denver, CO	NA	TSP	1978	27 ± 12%		6
Mueller et al. [1982]	Anaheim + Azusa, CA	urban	TSP	1977–1978	30–67%		96
Sempere and Kawamura [1994]	Tokyo	urban	TSP	1992	28–55%		4
Zappoli et al. [1999]	central Sweden	background site	$PM_{1.5}$	1996	60–83%	69–95%	5
Zappoli et al. [1999]	Hungary	rural	$PM_{1.5}$	1996	42–46%	48–50%	5
Zappoli et al. [1999]	N. Italy	urban	$PM_{1.5}$	1996	42–56%	55–80%	6
Facchini et al. [1999]	Po Valley, Italy	industrial + agricultural	$PM_{1.5}$	Nov. 1996 to March 1997	10–69%	11–72%	17
Narukawa et al. [1999]	Southeast Asia	under influence of Indonesia forest fire	$PM_{2.1}$	1997	5–32%		23
Ruellan et al. [1999]	central Africa	Boundary layer	TSP	Nov. 1996		46 ± 9%	11
		Harmattan layer				85 ± 18%	3
Decesari et al. [2001]	Po Valley, Italy	industrial + agricultural	$PM_{1.5}$	1996	55%	58%	1
Decesari et al. [2001]	Po Valley, Italy	industrial + agricultural	$PM_{1.5}$	Jan. 1998 to May 1999	41%	45%	40
Krivacsy et al. [2001a]	Jungfraujoch, Switzerland	background site	$PM_{2.5}$	summer 1998	46%	52%	8
Krivacsy et al. [2001b]	Jungfraujoch, Switzerland	background site	$PM_{2.5}$	summer 1998	47 ± 10%	60%	8
Krivacsy et al. [2001b]	K-puszta, Hungary	rural	$PM_{1.0}$	summer 1998	57 ± 9%	65%	22
Krivacsy et al. [2001b]	Mace Head, Ireland	marine	TSP	summer 1998	40 ± 5%	41%	5
Ruellan and Cachier [2001]	Paris	roadside			7–19%		
Mayol-Bracero et al. [2002]	Rondônia, Brazil	under influence of biomass burning	$PM_{2.5}$	Oct. 1999	42–70%	45–75%	10
J. Z. Yu et al. (manuscript in preparation, 2004)	Jeju, Korea	rural	$PM_{2.5}$	23 March to 30 April 2001	49–55%	64–68%	4
Yu [2002]	HKUST, HK	semirural	$PM_{2.5}$	Feb. 2001	27–61%	31–73%	11
				July 2001	22–51%	40–64%	10
Yu [2002]	Hok Tsui, HK	rural	$PM_{2.5}$	Nov. 2000 to Oct. 2001	33–46%	49–64%	4
Yu [2002]	Tsuen Wan, HK	urban	$PM_{2.5}$	Nov. 2000 to Oct. 2001	14–26%	29–45%	4
Yu [2002]	Mong Kok, HK	roadside	$PM_{2.5}$	Nov. 2000 to Oct. 2001	5–11%	14–26%	4

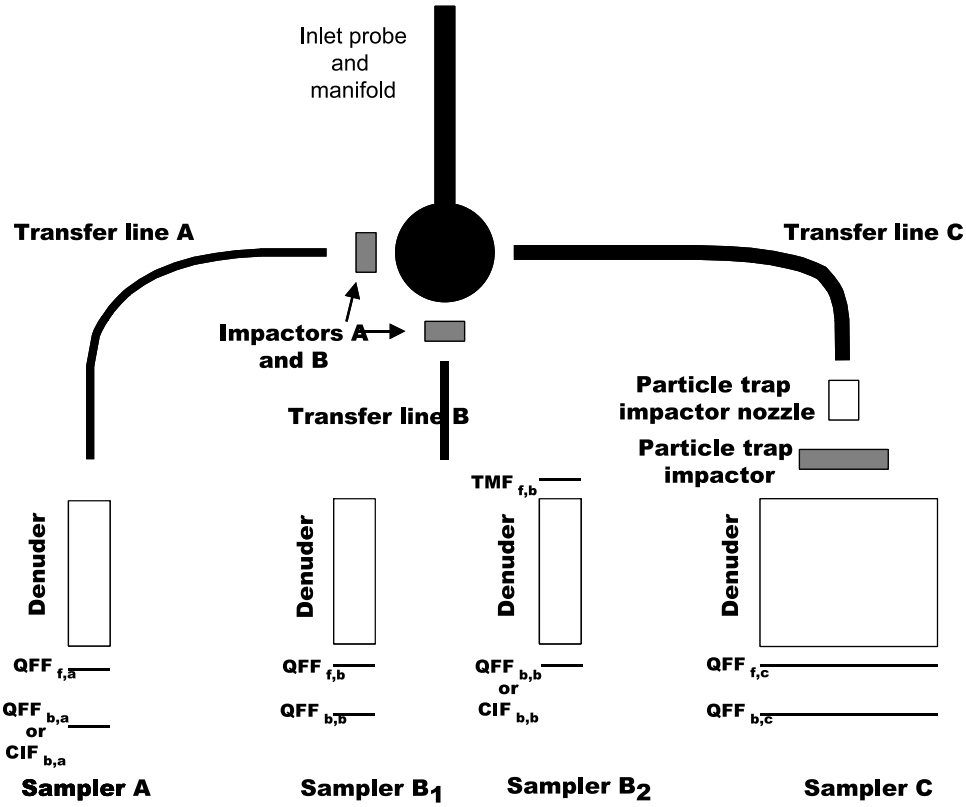

Figure 1. Schematic of the Twin Otter sampling inlet and denuder samplers used for the collection of carbonaceous aerosols during ACE-Asia.

stacked filter punches (1.45 cm^2 in size) under a stream of 1% O_2 and 99% ultrahigh-purity He while heating the sample in two temperature steps of 1 min at 600°C, and 2 min at 870°C.

[14] On the basis of the OC, EC, and TC contents of particles present on 1.45 cm^2 portions of the filters, it was determined that some filters had to be combined so as to achieve the detection limits of the analytical method used for molecular speciation. Filters collected under similar conditions were combined. For three flights the OC loading on the filter was sufficient and these filters did not need to be combined. There were three single-filter and three composite samples; a synopsis of the filters and composites is listed in Table 3. A description of how the type of atmospheric layer encountered was identified is given by *Mader et al.* [2002] and is based on measured profiles of temperature, relative humidity, particle number concentration, scattering coefficient at 450, 550 and 700 nm and Angstom exponent, *å*, during the particular RF.

4. Water-Soluble Organic Carbon (WSOC) Analysis

[15] Before the individual filters were combined into the composites, each filter was cut into two portions. The two

Table 3. Synopsis of the Single-Filter and Composite Samples

Filters	Synopsis of Sampling Conditions	Average Altitude, m	Maximum Altitude, m	Minimum Altitude, m
Flight 7	dust in sample, observed carbonate in OC/EC analysis; fly legs in East China Sea just east of Cheju Island, rendezvous with R/V *Ron Brown*; layer at 8000′ below 5500′ very high CN counts and large particles as well; well-mixed MBL	1024	3038	33
Flight 12	dust in sample, observed carbonate in OC/EC analysis; also flew through pollution layer; fly along 133 north of Oki Island to 38 N, fly 1 hour legs at 100′ and 6000′; an inversion at 6000′ and a dust/pollution layer below inversion; complete three spirals and two flat descents, good radiative data in gradients no cloud; prime closure candidate	1243	3705	25
Flight 17	pollution layer dominated; polluted marine boundary layer	104	197	27
Flights 11, 16, 18	multiple layers, but pollution layer dominated	1386	3710	31
Flights 3, 4, 5, 6	multiple layers sampled, observed dust during flights, all flights over Sea of Japan NE of Oki Island	1952	3826	30
Flights 2, 8, 14, 15	multiple layers, all samples near Kyushu	1006	2583	28

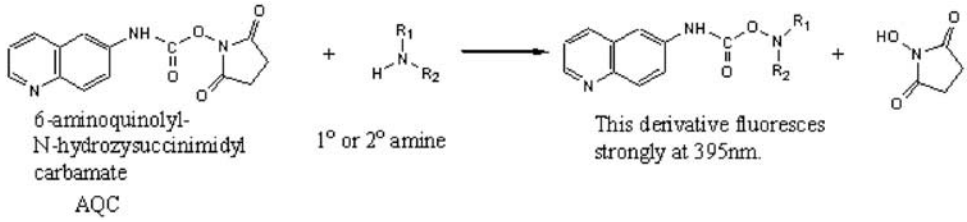

Figure 2. Derivatization reaction of $-NH_2$-containing compounds to form fluorescent derivatives.

portions were approximately 3/4 and 1/4 of the filter, respectively. The exact percentage of each portion was determined by weighing both portions using a microbalance. The 3/4 filter portions were combined to form the three composites. The remaining 1/4 filter was reserved for TC analysis by a thermo-optical OC/EC analyzer as described in section 3. Each 3/4 filter was extracted with 25 mL of high-purity water in a sonication bath for 20 min. The supernatant solution was filtered into a 250 mL flask using a syringe filter. The same 3/4 filter was extracted once more with 15 mL of water. The filtrate from this second extraction was reused for the second extraction of other 3/4 filters in the same composite to minimize the volume of the resulting composite water extract. The water extracts of the filters in the same group were combined. Composite F consisted of the highest number (i.e., 4) of individual 3/4 filters. Its combined water extract volume reached ~115 mL, the highest among all the composites. Additional water was added to other composite samples to make their final volumes 115 mL before reduction of water volume. The water extracts were reduced to ~8 mL using a rotary evaporator, and transferred to a 10.0 mL volumetric flask. Two portions of 1 mL water were used to rinse the rotary-evaporation flasks and then combined with the parent water extracts. The preanalysis final volume of each composite water extract was made to be 10.0 mL. Portions of the 10.0 mL water extracts were then used for the determination of WSOC concentrations and its speciation analysis. The backup filters were also combined and extracted to produce seven composites. Two blank water extracts were prepared following the same procedure using the two field blank filters. The WSOC levels in the samples were 3 times or higher than the average WSOC level of the blank water extracts. The concentrations of WSOC and individual WSOC species were all subtracted blank contributions. WSOC concentrations were measured using a total organic carbon analyzer (Model TOC-5000A, Shimadzu, Kyoto, Japan) [*Yang et al.*, 2003]. The recoveries of the water extraction step for the target classes of water-soluble organic compounds have been determined and reported in a previous study [*Yang et al.*, 2003]. The recoveries were in the range of 83–104%, indicating the extraction procedure and subsequent preanalysis treatments were quantitative.

5. Analysis of Amino Acids and Aliphatic Amines

[16] The amino acids and aliphatic amines both contain the $-NH_2$ functional group. As a result, both can be analyzed using Waters' AccQ-Tag method [*Cohen and Michaud*, 1993]. The amine group reacts with 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) to produce stable fluorescent derivatives that fluoresce strongly at 395 nm (Figure 2). The resulting derivatives of various amino acids and aliphatic amines can be resolved on a HPLC column using gradient elution of three eluents: acetonitrile, water, and phosphate buffer. Besides free amino acids, proteinaceous materials, which consist of two or more amino acid units, could be present in the ambient aerosols. For example, *Likens et al.* [1983] detected such material in rain samples. The proteinaceous materials can be regarded as combined amino acids and measured as their compositional amino acids through conversion to the free amino acids by hydrolysis.

6. Analysis of =OH-, =COOH-, and Carbonyl-Containing Compounds

[17] Two analytical procedures were used for $-$OH-, $-$COOH-, and carbonyl-containing compounds. The first procedure targets those containing only $-$COOH or $-$OH functional groups. A portion from each water extract is blown to dryness under a gentle stream of N_2, followed by sylilation using BSTFA and GC/MS analysis. The second analytical procedure targets those compounds containing at least one carbonyl group. Examples include glyoxal, methyl glyoxal, pyruvic acid, and glyoxylic acid. A portion from

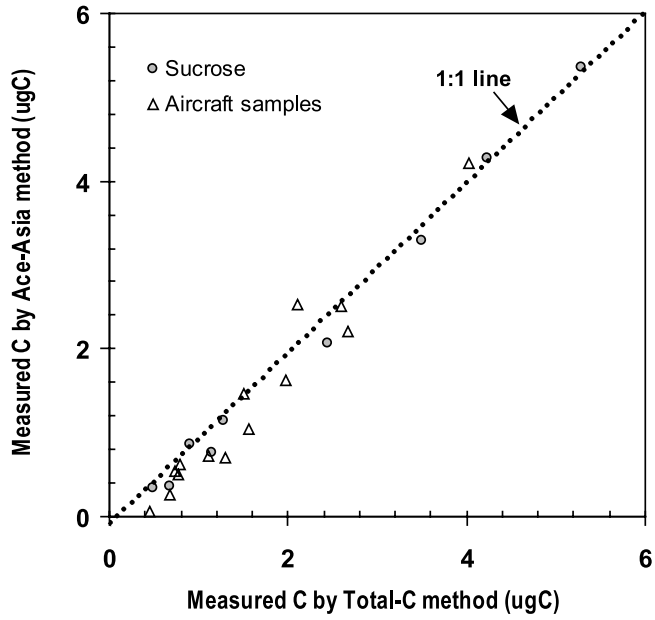

Figure 3. Comparison of TC measurements by the ACE-Asia and the Total-C temperature programs.

Table 4. Concentrations of TC and WSOC in the Samples

Sample	Flights	Sample Air Volume, m^3	TC, $\mu g\ C\ m^{-3}$	WSOC, $\mu g\ C\ m^{-3}$	WSOC/TC, %
A	F7	46	7.9	1.48	19
B	F12	62	4.6	0.54	12
C	F17	39	14.2	7.23	51
D	F11 + 16 + 18	116	6.7	3.15	47
E	F3 + 4 + 5 + 6	184	3.1	0.73	24
F	F2 + 8 + 14 + 15	152	4.4	1.20	27
Maximum			14.3	7.2	51
Minimum			3.5	0.5	12

each water extract is mixed with 2,3,4,5,6-pentafluorobenzyl hydroxy amine (PFBHA), extracted with dichloromethane, blown to dryness, and finally mixed with BSTFA. The resulting mixture is then analyzed using a GC/MS.

7. TC and WSOC

[18] The method using the Total-C temperature profile had two advantages over that using the ACE-Asia method. First, the carbon loadings in the case of using the Total-C method were 2–3 times those using the ACE-Asia method because 2–3 times as much filter materials were used in the Total-C method. Second, the Total-C temperature program was 190 s long whereas the ACE-Asia program was 605 s long. The shorter analysis time in the Total-C method resulted in narrower C peaks. It is plausible to expect that this would lead to better measurement precision and lower method detection limit (MDL). The MDL of the TC method was determined to be 0.22 μg C, half the MDL of the ACE-Asia method. A comparison of the TC levels on aircraft samples and sucrose standards as measured using the two methods is shown in Figure 3. Agreement between the two methods was reasonable at a concentration level of >2 μg C, but degraded as the level approached the MDL of the ACE-Asia method. On the basis of the above consideration, it was judged that the TC measurements by the Total-C temperature program were used for subsequent calculations.

[19] The TC concentrations for the composites could be computed using the TC loading on each individual filter and the fraction of each filter used for composing. Table 4 lists the TC concentrations for each composite. The TC concentrations varied from 3.1 to 14.2 μg C m^{-3}. The highest concentration of TC was observed for the sample collected during RF 17, which is noted in Table 3 as being collected in a pollution layer. In the study by *Mader et al.* [2002], samples collected during RF 17 had the highest OC, EC, and hence TC, levels of any of the Twin Otter flights during ACE-Asia, and modeled back trajectories suggested that the a pollution layer originating over China was sampled during RF 17. Sample D was a composite sample also collected primarily from a pollution layer; it had the third highest amount of TC of the six samples. Sample D was a composite that contained samples from RF 16 and 18. *Mader et al.* [2002] had observed that the air parcels sampled during RF 16 and 18 originated from same region of China, and the airmass encountered during RF 18 also spent time over South Korea. Sample A had the second most TC of the six samples but was not apparently collected from a layer identified as a pollution layer. RF 7 was influenced by dust; carbonate was detected in samples from this flight [*Mader et al.*, 2002]. Any carbonate in the sample would have contributed to the amount of TC measured for this sample, and this may explain why it had more TC than might have been expected for a sample not collected from a pollution layer.

[20] The method limit of detection (MLD) for WSOC was 0.88 ppm C [*Yang et al.*, 2003] and was determined as the concentration level corresponding to three times the standard deviation of five measurements of water extracts of blank filters. The blank WSOC level was on average 1.92 ppmC. This limit translated to atmospheric WSOC concentrations ranging from 0.05 to 0.22 μg C m^{-3} in the air volumes varying from 41 to 187 m^3 for the composites. The WSOC levels in the backup filter composites were all below 2 times the MLD, and two composites were below the MLD. It was therefore decided that no speciation would be carried out on the backup filter composites. WSOC concentrations in the front filter composites are listed in Table 4. They ranged from 0.54 to 7.23 μg C m^{-3}. The WSOC fraction contributed from 12 to 51% of the carbon mass. Samples C and D had about 50% of carbon mass attributed to WSOC. As discussed previously, the two samples were obtained from primarily pollution layers (Table 3). It is also interesting to note that although sample

Table 5. Concentrations of Organic and Inorganic Ions in Filter Samples[a]

Sample	Formate	Acetate	Lactate	MSA	Oxalate	Malonate	Maleate	Succinate	Glutarate	ΣOrganic Ions	ΣOrganic Ions/WSOC,[b] %	SO_4^{2-}	NO_3^-
A	23	23	97	11	122	20	9	0	8	313	6.9	3878	1582
B	29	51	2	29	140	26	0	32	21	331	19	3361	2097
C	219	131	44	40	634	111	22	65	69	1334	5.6	6984	4734
D	92	87	133	14	228	51	6	29	27	667	6.9	5164	1424
E	12	23	11	11	172	23	3	17	12	284	12	4140	355
F	27	19	48	14	165	29	5	14	17	337	8.7	3618	1164

[a]Concentrations are given in ng m^{-3}.
[b]The sum of the organic ions is the sum of the concentration expressed as μg C m^{-3}.

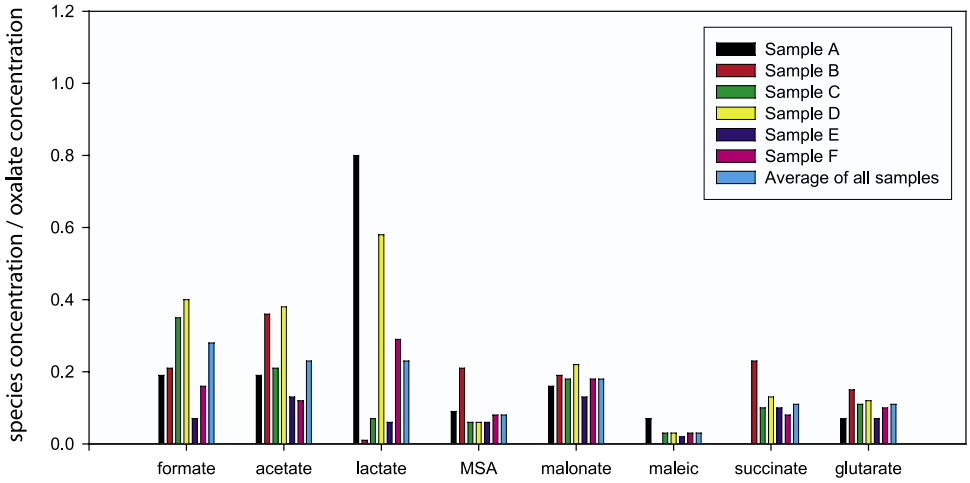

Figure 4. Profiles of the ratio of the concentration of individual organic ions (ng m^{-3}) to the concentration of oxalate (ng m^{-3}) as observed in the WSOC fraction of particles collected by the Twin Otter during ACE-Asia.

A had an amount of TC similar to that observed from samples taken from pollution layers (i.e., samples C and D), WSOC comprised only 19% of TC, significantly lower than the 50% observed for samples C and D. WSOC was extracted from the samples using water having a pH near 7, it has not been shown in laboratory studies that native aerosol carbonate present on filters would be fully dissolved into this water, nor has it been shown that dissolved carbonate would remain in the water extract prior to analysis by the Total-C method. If the native aerosol carbonate is not extracted into the water extract, or delivered to the TOC analyzer with 100% efficiency, the ratio of WSOC to TC would be lower for a sample influenced by dust, supporting the assertion that some of the TC observed in sample A was from carbonate collected from the dust layer. *Mader et al.* [2002] estimated that on average for the samples containing CC, CC comprised from 6 to 52% of total carbon and averaged 18%. This was considered a conservatively low estimate since a significant fraction of the total mass of atmospheric CC could be present on particles larger than 2.3 μm diameter, and it was not shown experimentally that particles of such a diameter could be transferred with 100% efficiency through the aircraft inlet and onto the filter.

8. Organic and Inorganic Ions

[21] Concentrations of organic and inorganic anions were determined using ion chromatography (IC) (Table 5). The organic anions detected included formate, acetate, lactate, methanesulfonate, and the ionic form of oxalic, malonic, maleic, succinic, and glutaric acid. The IC method could not differentiate the free acid and its dissociated ion; consequently, the concentrations represented the sum of the two forms for any acidic species. The ionic form of C_2–C_5 dicarboxylic acids (i.e., oxalate, malonate, maleate, succinate, and glutarate) were not detected in the blank samples whereas their presence was unambiguously detected in the samples, with the exception of maleate in sample B. The

Table 6. Concentrations of Dicarboxylic Acids and Inorganic Ions as Measured in Previous Field Studies[a]

		Dicarboxylic Acids					Inorganic Ions	
Location	Reference	Oxalic	Malonic	Maleic	Succinic	Glutaric	SO_4^{2-}	NO_3^-
ACE-Asia Twin Otter	this manuscript	244	43	7.5	26	26	4524	1893
ACE-Asia Twin Otter	*Gao et al.* [2003]	210	47		48	14.6	4602	12297
Antarctic	*Kawamura et al.* [1996a]	3.1	0.4		5.8	0.6		
Arctic	*Kerminen et al.* [1999]	23	17		24	6.3	780	
Arctic	*Narukawa et al.* [2002]	22	4.14	0.51	2.61	1.05		
Arctic	*Kawamura et al.* [1996b]	13.6	2.46		3.73	0.9		
Schenectady, NY	*Khwaja* [1995]	231	84		118			
Central Europe free troposphere	*Limbeck and Puxbaum* [1999]	153	22		14	2.7		
South Africa	*Limbeck et al.* [2001]	79	52		13	2		
South Africa savanna	*Limbeck et al.* [2001]	193	142		58	8.8		
Vienna	*Limbeck and Puxbaum* [1999]	340	244		117	26		
Hungary	*Kiss et al.* [1997]	131	29.9		33.3			
Tokyo	*Kawamura and Ikushima* [1993]	270	55	5.6	37	11		
Tokyo	*Sempere and Kawamura* [1994]	1352	322		279	81		
Los Angeles	*Rogge et al.* [1993]	NA	33		66	32		

[a]Concentrations are given in ng m^{-3}.

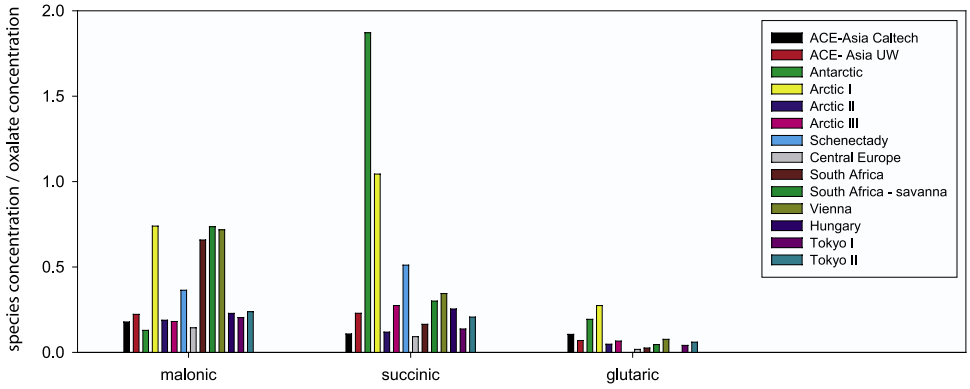

Figure 5. Profiles of the ratio of the concentration of individual organic ions (ng m^{-3}) to the concentration of oxalate (ng m^{-3}) as identified in carbonaceous aerosols collected at numerous sites. ACE-Asia UW [*Gao et al.*, 2003]; Antarctic [*Kawamura et al.*, 1996a]; Arctic I [*Kerminen et al.*, 1999]; Arctic II [*Narukawa et al.*, 2002]; Arctic III [*Kawamura et al.*, 1996b]; Schenectady, New York [*Khwaja*, 1995]; Central Europe [*Limbeck and Puxbaum*, 1999]; South Africa [*Limbeck et al.*, 2001]; South Africa savanna [*Limbeck et al.*, 2001]; Vienna [*Limbeck and Puxbaum*, 1999]; Hungary [*Kiss et al.*, 1997]; Tokyo I [*Kawamura and Ikushima*, 1993]; Tokyo II [*Sempere and Kawamura*, 1994].

level of methanesulfonic acid (MSA) in all samples was higher than 3 times that in the blank samples. The levels of formate, acetate, and lactate were all higher than the respective blank levels; however, only three out of the six samples had levels over 2 times the blank levels. The sum of all the detected organic ions (expressed in units of μg C m^{-3}) accounted for 6–19% of the WSOC mass.

[22] In the six samples collected by the Twin Otter during ACE-Asia, of the organic ions observed in the WSOC fraction, oxalate had the highest concentration. For each sample the concentration of each organic ion observed in the WSOC fraction was normalized by the concentration of oxalate (Figure 4). Interestingly, the only feature differentiating the pollution-influenced samples collected from air parcels originating from mainland China (i.e., samples C and D) from the other samples is that the ratio of formate to oxalate was a slightly higher in these samples as compared to the others. Sample D also shows a large enrichment of lactate and a slight enrichment of acetate. The profiles of the dicarboxylic acids were rather similar among the samples. It is not immediately clear why samples A and D are both enriched in lactate; however, it is possible that the relatively high ratio of lactate to oxalate is a signature of some currently unidentified source of carbonaceous aerosol. Sample B also stands out from the other samples with a relative enrichment of acetate, MSA, succinate, and glutarate in these samples as compared to the other six. Sample B was collected during RF 12, and *Mader et al.* [2002] observed that in samples collected during RF 12 carbonate carbon was detected while at the same time measurements of the Angstrom exponent (*å*) were between 1.5 and 1.9. On the basis of these observations, *Mader et al.* [2002] suggested that for RF 12 sampling was conducted in a layer consisting of a mixture of dust and pollution.

[23] Dicarboxylic acids have been observed in particulate samples collected in several previous studies (Table 6). In the majority of these studies, of the dicarboxylic acids observed, oxalate was observed at the highest concentration. Note when comparing the studies listed in Table 6 it is important to note that in these studies samples were collected on filter samplers whereas the samples collected in this study were obtained using a denuder sampler. It is possible that some differences among these sites could be due to differences in sampler configuration and analytical methods employed. As in Figure 4, the concentration of the each dicarboxylic acid was normalized by that of oxalate, and these data are summarized in Figure 5. On the basis of a comparison of the profiles shown in Figure 5, the ACE-Asia samples were most similar to the Tokyo samples and two of the Arctic samples. There are distinct differences between the ACE-Asia samples and the Antarctic and the Arctic samples collected by *Kawamura et al.* [1996a, 1996b] and

Table 7. Concentrations of Free Amino Acids, Combined Amino Acids, and Aliphatic Amines in the Composites[a]

Sample	CAA + FAA, ng m^{-3}	Aliphatic Amine, ng m^{-3}	Σ(CAA + FAA + Aliphatic Amine)/WSOC,[b] %
A	56.5	3.4	1.6
B	49.5	5.1	4.2
C	274.4	24.5	1.6
D	145.5	8.8	2.0
E	66.8	3.7	4.0
F	51.3	3.9	1.8

[a]FAA, free amino acids; CAA, combined amino acids.
[b]The concentrations of CAA, FAA, and aliphatic amines are expressed as μg C m^{-3}.

Table 8. Individual Total Hydrolyzable Amino Acids (i.e., Free and Combined Amino Acids)[a]

Amino Acid	Sample					
	A	B	C	D	E	F
Glycine	274.4	223.5	1567.6	610.0	205.1	261.7
Alanine	61.1	60.0	198.4	112.2	46.2	51.7
Proline	40.3	66.1	105.9	60.9	39.7	49.2
Cystine	2.1	26.1	164.2	67.1	24.2	29.4
Threonine	39.1	0.0	134.3	84.8	79.8	0.0
2-Alanine	28.3	41.1	117.9	54.7	24.6	32.7
Glutamic acid	28.6	0.2	94.4	84.5	42.5	8.5
Aspartic acid	16.6	0.0	73.9	73.8	15.2	5.6
Valine	17.7	14.1	56.3	30.2	16.8	11.6
Serine	12.7	0.0	48.9	53.2	29.0	2.4
2-Aminobutyric acid	9.4	12.1	43.2	20.7	8.0	8.8
Lysine	11.3	6.4	19.9	38.7	18.5	6.4
Leucine	3.6	22.9	4.0	24.4	20.0	14.2
Galactosamine	15.6	7.1	96.5	5.5	6.6	15.4
Tyrosine	6.7	12.9	56.0	30.7	10.4	11.2
Ornithine	6.3	10.8	19.8	19.3	16.3	13.5
Isoleucine	4.4	5.3	20.4	16.0	9.3	3.8
Phenylalanine	0.9	2.0	13.7	13.7	7.4	2.2
Histidine	0.0	0.0	15.6	14.1	6.7	1.3
Methionine	0.0	0.0	0.0	11.5	0.0	0.0
Arginine	0.0	0.0	0.0	0.0	0.0	0.0

[a]Concentrations in pmol m^{-3}.

Kerminen et al. [1999], respectively. These differences are mostly due to the relative enrichment in succinic acid in those samples. There were additional differences between the ACE-Asia samples and those from Vienna and South Africa, primarily in the relative amount of malonic acid.

[24] Two major inorganic species, sulfate and nitrate, were determined simultaneously with the organic ions. Chloride was not quantified because of contamination caused by the use of an ice NaCl solution as a coolant during rotary evaporation. The sum of the masses of the two identified inorganic ions exceeded the sum of the mass of the identified organic ions by a factor of 9 to 17.

9. Amino Acids and Aliphatic Amines

[25] Table 7 lists the concentrations of free and combined amino acids and aliphatic amines in the six samples. The dominant amino acids and amines in the samples had levels more than more than three times those present in the blank. Their relative contribution to the carbon mass in the WSOC fraction ranged from 1.6 to 4.2%. Concentrations of the individual amino acids are presented in Table 8. Glycine was the most abundant amino acid species, accounting for approximately one-half of the total amino acids. Alanine, proline, cystine, and threonine are next abundant, each accounting for more than 5% of the total amino acids. Three aliphatic amines, methyl amine, ethyl amine, and ethanol amine, have been identified to be present in each composite sample. Among the three, methyl amine is the most abundant. The concentrations of the individual amines were normalized by the concentration of glycine, and the profiles for the six samples are shown in Figure 6. There were no distinguishing features among the type of samples; that is, the samples taken from pollution layers could not be distinguished from other samples. Several amino acids exhibit a similar profile among all six samples. For example, among all six samples the profiles of alanine, proline, 2-alanine, and galactosamine had similar profiles, as well as serine, lysine, isoleucine, phenylalanine. It is likely that all the amino acids in a given group may have been combined in a single proteinaceous material that was hydrolyzed during the analysis.

10. −OH-, −COOH-, and Carbonyl-Containing Compounds

[26] In Table 9 the concentrations of the individual −OH- and −COOH-containing compounds determined above the method detection limit are listed. Some compounds observed at levels lower than the method detection limits were not quantified; these include benzoic acid, azelaic acid, and C_3 to C_5 dicarboxylic acids. The quantification of oxalic acid using this GC method suffers from poor precision due to evaporative loss during the sample pretreatment. The IC method is more reliable and has better sensitivities for the determination of C_2−C_5 di-acids. Of compounds that contain one or more carbonyl groups, glyoxal, methyl glyoxal, glyoxylic acid, and pyruvic acids, some were observed above the method detection limit only in samples C and

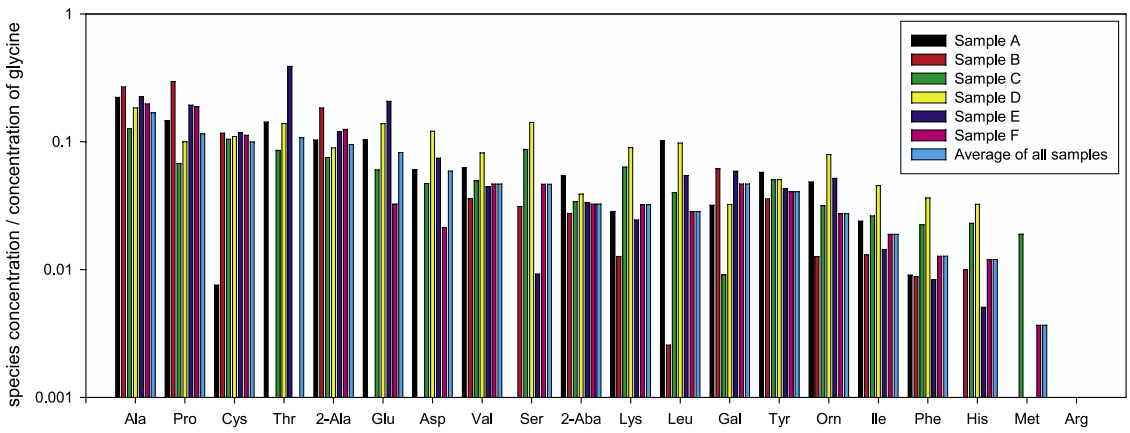

Figure 6. Profiles of the ratio of the concentration of individual amino acids to the concentration of glycine (ng m^{-3}) as observed in the WSOC fraction of particles collected by the Twin Otter during ACE-Asia.

Table 9. Concentrations of Compounds Containing −OH and −COOH Groups[a]

Sample	Glycolic	Glycerol	Phthalic	Levoglucosan	Σ(OH + COOH)	Σ(OH + COOH)/WSOC[b]
A	5.2	6.8	8.8	11.2	31.9	1.0%
B	11.0	6.8	5.6	12.6	36.0	2.8%
C	51.8	8.2	43.0	78.5	181.5	1.1%
D	15.6	4.0	8.4	65.8	93.8	1.3%
E	4.5	6.0	5.9	7.0	23.4	1.4%
F	9.0	3.0	7.2	13.5	32.8	1.2%

[a]Concentrations are given in ng m^{-3}.
[b]Σ(OH + COOH) is expressed as μg C m^{-3}.

D, which were collected from primarily pollution layers. It is not necessarily the case that these compounds are unique to pollution layers; rather, such layers had sufficiently high levels of WSOC such that, for the given amount of sampling time, it was possible to collect enough material to meet the method detection limits. Concentrations of the individual −OH- and −COOH-containing compounds were normalized by the concentration of WSOC and the profiles for the six samples are shown in Figure 7. As compared with the other four samples, those collected from the pollution layers had a relatively lower amount of glycerol. Levoglucosan is a tracer for wood combustion [*Simoneit et al.*, 1993]. *Fine et al.* [2002] measured the emission rates of total carbon as well as several individual organic compounds (including levoglucosan) from the burning of six different wood species. Using data from these studies, it was observed that levoglucosan comprised, on average, 4.4% of total carbon mass (where the mass of total carbon and levoglucosan was expressed in units of μg C.). All samples collected during ACE-Asia had detectable amounts of this compound. In these samples levoglucosan comprised from 0.1 to 0.4% of total carbon mass (where the mass of total carbon and levoglucosan was expressed in units of μg C.). Comparing these ratios to those obtained from the controlled burning of different wood types [*Fine et al.*, 2002] and assuming (1) that levoglucosan is a conservative tracer for biomass burning and (2) that the ratio of levoglucosan to total carbon in aerosols present at the source of the biomass emissions from eastern Asia is similar to the average value measured by measured by *Fine et al.* [2002], the data suggest that perhaps ≈2–10% of the carbonaceous aerosol mass collected during ACE-Asia had originated from biomass burning. Sample C (obtained 27 April) had a ratio of levoglucosan to total carbon of 0.2% (μg C/μg C). Using the same approach as discussed above, our data suggest that ≈5% of the total carbonaceous aerosol mass originated from biomass burning. For samples collected on the same day, *Gao et al.* [2003] used positive matrix factorization analysis to show that ≈5–10% of the total carbonaceous aerosol mass originated from biomass burning.

11. Conclusions

[27] Organic aerosol molecular compositions measured in airborne filter samples during the ACE-Asia field campaign are presented. Particular attention is paid to identification of water-soluble organic carbon fraction. A variety of analytical techniques has been applied to the samples, including gas chromatography/mass spectrometry, ion chromatography, and high-pressure liquid chromatography. The current paper presents, as well, a reasonably complete summary of previous determinations of WSOC composition of atmospheric aerosols. The present results, in terms of compounds identified and ratios of WSOC to total particulate carbon, are generally consistent with those of previous studies carried out in other areas of the globe. Therefore the current work adds to the growing base of organic aerosol molecular composition data. As in previous atmospheric sampling of

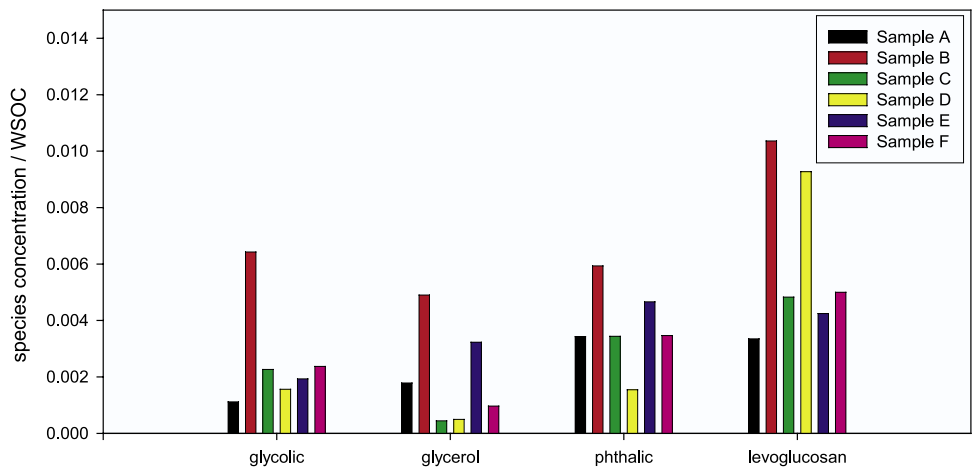

Figure 7. Profile of the ratio of the concentration of −OH- and −COOH-containing compounds (ng C m^{-3}) to the concentration of WSOC (ng C m^{-3}) as observed in the WSOC fraction of particles collected by the Twin Otter during ACE-Asia.

particulate organic compounds, only a fraction of the organic compounds present were identified. Development and application of analytical techniques that allow substantial identification of the suite of compounds present remains a significant challenge.

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